

MOLECULAR DYNAMICS STUDY OF SLIDING MECHANISMS OF NI, AMORPHOUS NI-P AND NANOCRYSTALLINE NI FILMS

ANDREY I. DMITRIEV^{1,2}, ANTON YU. NIKONOV^{1,2} AND WERNER ÖSTERLE³

¹Institute of Strength Physics and Materials Science (ISPMS), Russian Academy of Science
Akademichesky pr. 2/4, 634021 Tomsk, Russia
e-mail: dmitr@ispms.tsc.ru, <http://www.ispms.ru/>

²National Research Tomsk State University (TSU)
Lenin pr. 36, 634050 Tomsk, Russia
<http://www.tsu.ru>

³Federal Institute for Materials Research and Testing
Unter der Eichen 87, Berlin, D-12200, Germany
<http://www.bam.de>

Key words: Amorphous film, nanocrystalline nickel, sliding simulation, molecular dynamics, deformation mechanism.

Abstract. In the paper by using molecular dynamics method we investigate the sliding feature of different nano-scale specimens: single-crystal nickel evolving from amorphous pure Ni during shear deformation, Ni-P a layer and nanocrystalline nickel. Special attentions are paid to the value of resistance stresses and plastic deformation mechanisms manifested during sliding simulations. The study is performed at an ambient temperature. The analysis showed that Ni-P amorphous structure is characterized by lowest resistance stresses and smooth sliding provided by the bond-switching mechanism between pairs of atoms due to shear loading. Similar low resistance stress was also observed for an amorphous pure Ni layer, but only at an early stage of sliding before crystallization occurred. The highest shear resistance was confirmed for single-crystal nickel caused by classical deformation mechanisms like stacking fault formation and dislocation movement. Sliding simulations of a nanocrystalline specimen show both, crystal defect driven deformation in the bulk and sliding along quasi-amorphous grain boundaries. Thus, it was shown that nickel-phosphorous coating in amorphous-like state may exhibit low friction properties, and, therefore, serve as the solid lubricant material.

1 INTRODUCTION

Pure metal coatings are highly appreciated in many technical applications due to relatively simple manufacturing technologies that allow adjusting the film properties depending on customers' needs, controlling the processing parameters. Compared to copper and tin coatings nickel is a hard coating which often is used to increase the load carrying capacity of a substrate and thus improve its wear resistance [1]. Frequently, the improvement of hardness and wear resistance could be attributed to a reduction of grain size of electro-plated nickel coatings [2]. Taking into account that the effect of grain size reduction on hardness and wear

resistance is described by the Hall-Petch relationship [3], the effect of the grain size on the coefficient of friction (COF) has not been sufficiently studied. Considering electro-plated nickel coatings, the above mentioned authors have observed a decrease of the COF with decreasing grain size [2]. Fan et al. explained the peculiar mechanical behavior of nanocrystalline materials by assuming a certain grain boundary (GB) layer adopting an amorphous structure [4]. Since interesting results were obtained recently by using MD-modeling for sliding simulations of amorphous silica and carbon films [5], the idea was born to study the sliding behavior of amorphous nickel films supported by nickel crystals on both sides in a similar way. With this model setup we hoped to find an explanation for the experimentally observed decrease in COF with decreasing grain size during the transition from the micrometer to the nanometer range [2].

Similar as nanocrystalline nickel coatings, completely amorphous films can also be used to reduce the friction coefficient of several tribological couples [6]. The amorphous structure is stabilized by adding a second element to the system that can interstitially dissolve in the matrix. Since this happens on the atomic scale at high temperature followed by rapid quenching, the metastable amorphous phase is preserved at ambient temperature. A well-known technical coating system is Ni-P which is produced by electro-less deposition from an electrolyte containing nickel salts and NaH_2PO_2 as reducing agent. The distinctive characteristics of the Ni-P coating include wear resistance, high hardness, excellent lubricating properties, and others. It is widely applied in aviation machine, chemical industry, electronic manufacturers and etc. [1]. Moreover, it was found recently [2] that the hardness of Ni-P coating depends on P content and crystallization time at the given temperature. According to experimental observations high P ($\text{P} > 6 \text{ \% vol.}$) coating has amorphous microstructure and it's characterized by high corrosion resistance and low friction properties.

The present paper focuses on a comparison of the sliding behavior of amorphous and nanocrystalline nickel films determined on the basis of MD modelling results. This study is related to interesting technical materials, namely the electro-less fully amorphous Ni-P coating and the electro-plated nanocrystalline glossy nickel coating. The objective of the work was to find correlations between the microstructure of different types of electro-plated nickel coatings and the friction forces evolving when coated parts were subjected to sliding.

2 EXPERIMENTAL BACKGROUND

The technical application of the considered tribological system is a plug-socket interconnects, where the plug is made of copper-Sn alloy coated with nickel and the socket is a printed circuit coated with copper. Since plug-in and plug-out forces have to fulfill certain requirements the tribological system has to be optimized. The first step into this direction is to determine coefficients of friction of different variants of nickel coatings sliding against copper by applying pin-on-disc tests in the laboratory. This was done in the meantime, and the results are shown in Fig.1.

Increasing friction forces are observed while sliding occurs in positive direction especially for nanocrystalline, but also for micron-sized and submicron-sized Ni after some cycles, but not for the amorphous Ni-P coating. Simultaneously observed friction force fluctuations and acoustic signals provide evidence that local cold welding with subsequent de-bonding has occurred between pin and disc material. The amorphous material on the other hand seems to

be not prone to cold welding with the counter body. Thus it turned out that understanding the different mechanisms of sliding of the amorphous and nanocrystalline material are key factors for optimization of the friction couple towards desired functional properties of the envisaged application, a plug-socket connection.

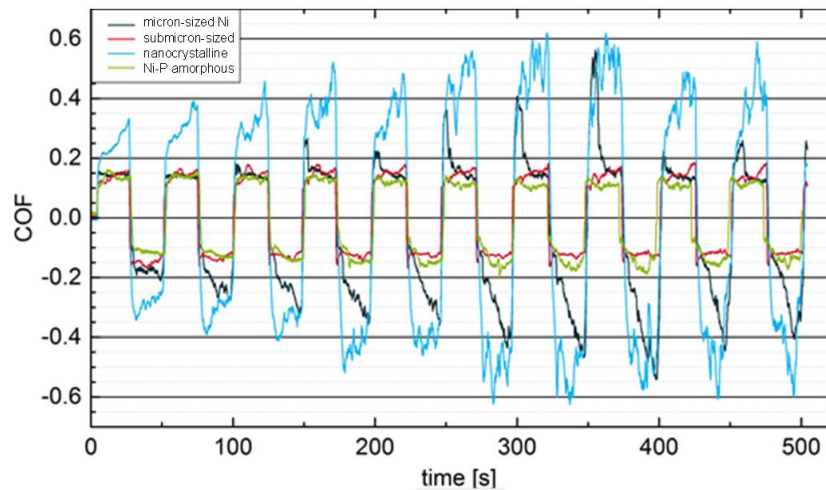


Figure 1: Results of reciprocating pin-on-disc tests; copper pins sliding against various nickel coatings.

3 THE NUMERICAL MODEL

Simultaneously with described above experimental studies a certain progress was made in sliding simulations of amorphous films by applying molecular dynamics modelling (MD) [7–9]. By the following a description of the numerical model is given in short. The MD simulation model of sliding test was consisted of three parts: the central part is a specimen under loading in shape of parallelepiped and two supports (loaded blocks) on top and bottom having an ideal single crystalline Ni structure. Each of the loaded blocks in turn was divided in an inner layer with Newtonian atoms and thin outer boundary layer with atoms through which the loading conditions were implemented. The vertical dimension of each loaded block was identical and was about 8 nm including the boundary layer thickness of approximately 1 nm as shown in Fig. 2a and Fig. 3a. The total dimensions of the specimen with both loaded blocks were 7 x 10 x 30 nm along Z-, X- and Y-axes respectively. Thus, the total number of atoms within the framework of a micro-canonical ensemble NVE was about 200000. Three different structures of the central part were considered: Ni in amorphous state and amorphous Ni-P. The simulation model for sliding test of nanoscale polycrystalline nickel had a slightly different structure and will be described later separately.

The modeled structure, situated between two stiff support layers, was subjected to a sliding simulation with constant velocities +15 and -15 m/s applied to the upper and lower boundary layers, respectively. Furthermore, additional compression forces along the Y direction corresponding to normal pressures of 350 MPa were applied to boundary atoms while the temperature of the whole specimen was kept in the acceptable range from 250 K to 350 K.

A periodic boundary condition is prescribed in the X- and Z-directions of the specimen to reduce the simulation scale effect. The atomic interactions between nickel atoms as well as between Ni and P atoms are described by the embedded atom method (EAM) potential [10].

All MD calculations were implemented using the LAMMPS [11] molecular dynamics code with a time step of 1×10^{-15} s. The common neighbor analysis (CNA) is adopted to identify the structural allocation of each atom during sliding simulation [12]. According to CNA, a single hexagonal-close-packed (hcp) coordinated-layer means a coherent twin boundary, the two hcp-coordinated-layers with a face-centered-cubic (fcc) coordinated-layer between them denote an extrinsic stacking fault, and the two adjacent hcp-coordinated-layers indicate an intrinsic stacking fault. Atoms with unidentified structure are denoted separately and indicate the amorphous-like structure. In this study, we track the microstructural evolution to reveal the features of shear deformation of specimens with different inner structure.

3 RESULTS FOR SPECIMENS WITH AN AMORPHOUS INTERLAYER

3.1 Sliding Simulation of Ni

A thin layer of amorphous nickel was produced by virtual heating and further quenching to 300 K of the middle part of an initially defect-free single crystal nickel specimen. Before start of loading, the specimen was relaxed to equilibrium configurations with minimum potential energy. Due to atoms rearrangement during melting and subsequent quenching procedures a few structural defects like nanopores and vacancy clusters were created in the amorphous layer as shown in Fig 1a where the initial structure is shown.

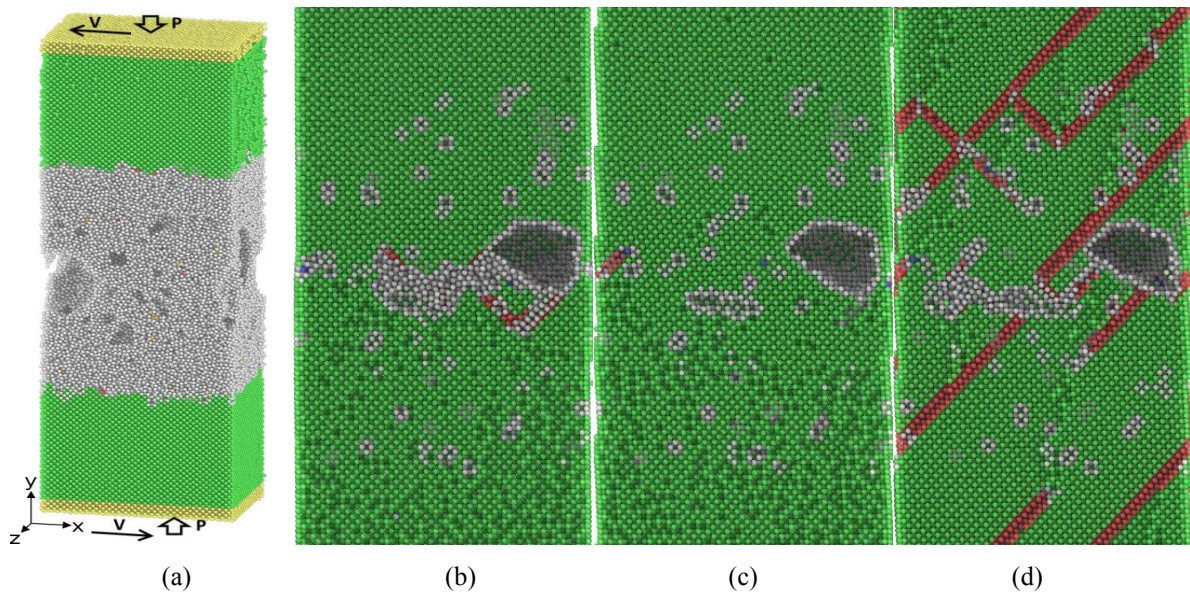


Figure 2: (a) The loading scheme and the initial structure of the modeled specimen before simulation of sliding. Structure (projection on XY plane) of an amorphous nickel layer at different moments of time: (b) after 30 ps; (c) after 70 ps; and (d) after 100 ps. Atoms are colored on the basis of values calculated by CNA. Green: fcc, red: hcp, gray: unidentified (amorphous). Yellow atoms shown in figure (a) belong to loaded layers.

Figure 2 also presents some snapshots of XY-projections of the microstructural evolution of the modeled specimen during the sliding simulation. For a clearer visualization of the microstructure evolution the central part of the modeled specimen initially containing an amorphous layer is shown only. Surprisingly, but anyway plausibly, the amorphous structure

did not remain stable during the sliding simulation. The onset of crystallization leads to an increase in resistance stress, as shown in Fig. 4a. This process is taking place during the first 30 ps for our specimen (see Fig. 2b). As shown in Fig. 2c, the crystallization of the amorphous layer can lead to formation of residual structural defects. Most atoms and their neighbors correspond to the fcc structure, but there are also some nano-pores, vacancies and nano-sized twins and intrinsic stacking faults corresponding to the hcp structure. The number of structural defects (nano-twins and stacking faults) increases with further loading (Fig. 2d).

3.2 Sliding Simulation of an Amorphous Ni-P Film

To study the features of sliding of an amorphous Ni-P film we extended the modeling system by adding 20 at. % P (11,65 wt. % P) to Ni amorphous interlayer. Similar to previous calculations we simulate a layered sample where two Ni crystals were separated by the central part, where atoms of Ni were initially mixed with atoms of P. An amorphous state of Ni-P layer was reached by virtual heating and further quenching to 300 K of that part of the modeled specimen. The resulting structure is shown in Fig. 3a. The thickness of the amorphous layer was about 14 nm.

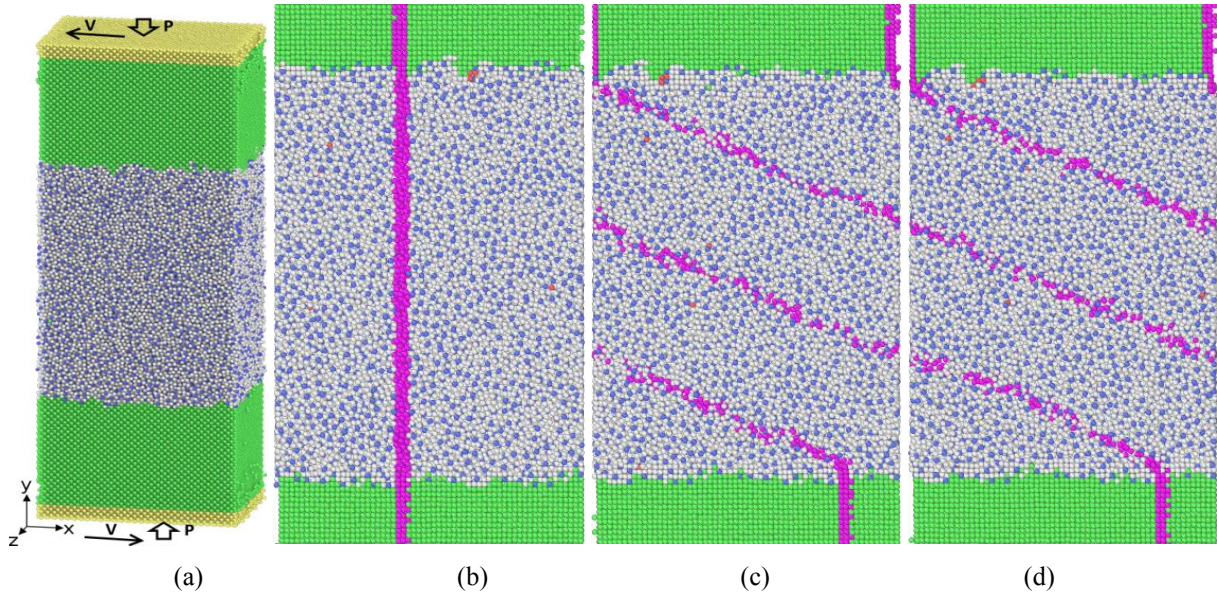


Figure 3: (a) The loading scheme and the initial structure of the modeled specimen before simulation of sliding. Structure (projection on XY plane) of a central fragment containing an amorphous Ni-20 at. % P layer at different moments of time (b) 0 ps; (c) after 500 ps and (d) after 1 ns. CNA values are used for atoms' colorization. Green: fcc Ni-atoms, blue: P-atoms, gray: undefined (amorphous) Ni atoms. A magenta marking is used to visualize atomic displacements in the specimen after corresponding time of sliding. The formation of several parallel lines is caused by the action of periodic boundary conditions along the direction of shear loading.

According to the results of simulation the structure evolution always show homogeneous shearing within the amorphous Ni-P interlayer, irrespective of the applied normal pressure. This is confirmed by the snapshots with atomic configurations at different time steps shown in the Fig. 3b-d. Thus, the results of MD-modeling predict smooth sliding and a low COF for the amorphous Ni-P layer.

4 SIMULATION RESULTS FOR NANOSCALE POLYCRYSTALLINE NI

4.1 Model Description

A further objective of our study was to estimate tangential stresses occurring during sliding simulations of nickel layers with nanocrystalline structure. The motivation was to explain significant differences of the tribological behavior observed experimentally for electro-plated nickel coatings and electroless deposited Ni-P coatings [13]. The modelled sample consisted of more than 1.5 million atoms with the following geometry: $40,5 \times 40,5 \times 10,5$ nm along X, Y and Z axis, respectively. To create the initial nanocrystalline nickel structure the Voronoi partition method was used [14]. In our simulation the crystallographic orientation of each Voronoi cell (grain) was chosen stochastically. The resulting polycrystalline Ni specimen has an average grain size of 8 nm. The structure after the relaxation stage is shown in the Fig. 5a where atoms are colored according to the values calculated by common neighbor analysis (CNA). For a clearer visualization of the defect structures atoms with local topology different from the fcc structure are depicted only. As a consequence of residual stresses due to polycrystallization after relaxation stage mostly all nano-grains contain structural defects like ensembles of vacancies or different planar defects as depicted in figure 4a. Phenomena like recrystallization and grain boundary curvature are also taking place.

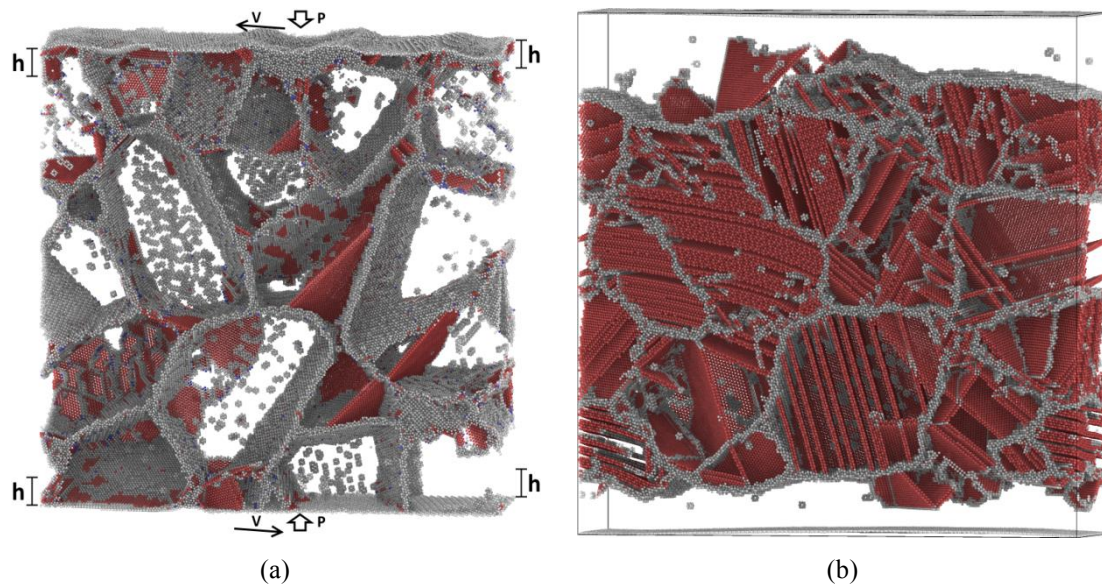


Figure 4: Structure of the modeled polycrystalline Ni specimen (a) after the relaxation stage and (b) after 750 ps of sliding. Atoms are colored on the basis of values calculated by CAN: Red atoms – hcp lattice; gray – unidentified configurations (border atoms, grain boundaries, vacancies and so on). Fcc atoms are not shown.

The loading scheme was implemented in the following manner. The atoms of the polycrystalline specimen belonging to top or bottom border layers with the thickness h of about 2 nm from each side were substituted by atoms of single-crystal nickel with defect-free structure of the same thickness. All atoms of these two layers were subjected to lateral motion with constant velocity. The velocity was oriented along X direction. Furthermore, top and bottom layers move in opposite directions with 15 m/s each. Thus the total relative velocity

was 30 m/s. The Z projections of atoms velocities in border layers were fixed to zero. Similar to amorphous Ni sliding simulation additional compression loading along Y direction of about 350MPa was applied to atoms belonging to boundary layers. Periodic boundary conditions were simulated along Z and X directions. The initial temperature was 300 K and during loading the temperature was controlled within the acceptable range from 250 K to 350 K.

4.2 Sliding Simulation of a Nanocrystalline Ni Layer

Figure 4b shows the nanocrystalline Ni structure after 750 ps of sliding simulation. Obviously, a lot of structural defects are formed within nano-grains as a consequence of shearing between the upper and lower boundary layers. Note however, that a major part of the stacking faults is just an expansion of “original” defects caused by the action of periodic boundary conditions and a particular crystallographic orientation of that nano-grain. During our sliding simulations two further structural changes are observed. Firstly, grains are rotated in a way that the number of horizontal GBs lying parallel to the sliding direction is increased. Secondly, the interface between monocrystalline loading blocks and the central nanocrystalline structure is changed. With increasing simulation time, corresponding to increasing sliding distance, the load bearing single crystal blocks grow by consuming nearest atoms of the inner polycrystalline structure. Thus stress-driven interface migration in the direction perpendicular to the lateral motion of the single crystalline support layers occurs.

5 COMPARISON OF TANGENTIAL STRESSES

In Fig. 5 tangential resistance stresses are compared for all three specimens considered above (single-crystal nickel evolving from amorphous pure Ni during the sliding simulation, Ni-P amorphous layer and nanocrystalline nickel). The resistance stress was calculated as a ratio of resistance force and contact area of the loaded layer whereas the resistance force was computed as resulting tangential force acting on all loaded atoms in that layer. As expected, the average value of resistance stress in case of the polycrystalline nickel specimen is lower than the corresponding parameter for the single-crystal case and about twice as high as for the Ni-P amorphous structure. In all cases an averaging consisted of calculation of the mean value of 100 neighbouring points.

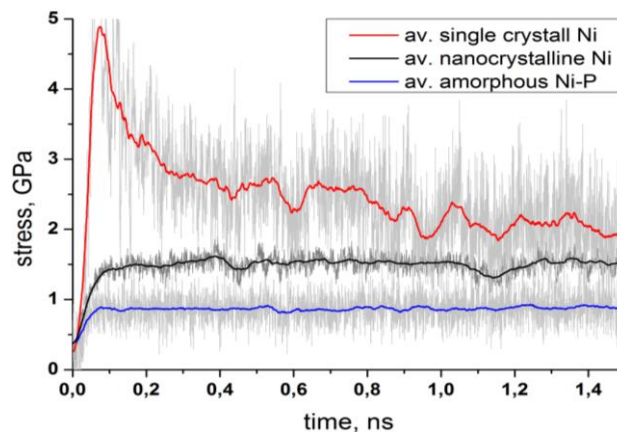


Figure 5: Time dependencies of resistance stress for the three modeled specimens. Light grey peaks denote instantaneous values and coloured curves represent the corresponding mean values.

6 CONCLUSIONS

Sliding simulations based on molecular dynamics modeling provided interesting insights into elementary friction mechanisms of amorphous and nanocrystalline nickel films which are widely used in numerous tribological applications. The experimentally observed low friction performance of an amorphous Ni-P coating [13] was confirmed by MD modeling. This behavior could be attributed to homogenous shearing of the amorphous film without defect formation. Smooth sliding is provided most likely by the bond-switching mechanism, which means that after breaking a bond between a pair of atoms due to shear loading, both atoms move a short distance in opposite directions before they are bound again to other atoms.

It has been shown that grain boundary atoms which could not be assigned to a crystallographic structure and thus can be considered as amorphous layers, play an important role during sliding simulations of nanocrystalline nickel. In that case, most of the shear deformation needed for accommodation of opposing sliding velocities is concentrated in horizontal grain boundaries. Both, grain boundary alignment and interface roughening increase with increasing sliding time. Since these mechanisms exert opposing effects on friction force, higher stresses are needed for initiating sliding of the nanocrystalline sample than for the amorphous structure stabilized with 20 at% P. Nevertheless, good tribological performance (low friction and wear) can also be expected for nanocrystalline nickel coatings because of the evidenced crucial role of GB-sliding. It should be mentioned here that the grain boundaries of the nanocrystalline sample, actually consisted only of an array of single unidentified atoms, and not of a several nanometer thick amorphous layer, as assumed by Fan et al. [4]. Even after plastic deformation, the grain boundary structure did not change. Only in the presence of certain alloying atoms a thickening of amorphous GB-layers was observed.

ACKNOWLEDGEMENTS

Investigations have been carried out with financial support from Program for Basic Scientific Research of the State Academy of Science on 2013–2020. The numerical simulations have been carried out with supported by Tomsk State University competitiveness improvement program.

REFERENCES

- [1] Wänstrand, O., Larsson, M., Kassman-Rudolphi, A. Mechanical and tribological properties of vapour deposited low friction coatings on Ni plated substrates. *Tribol. Int.* (2000) **33**:737-742.
- [2] Jeong, D.H., Gonzalez, F., Palumbo, G., Aust, K.T., Erb, U. The effect of grain size on the wear properties of electrodeposited nanocrystalline nickel coatings. *Scripta mater.* (2001) **44**:493-499.
- [3] Hall, E.O. Variation of hardness of metals with grain size. *Nature* (1954) **173**:948-949.
- [4] Fan G.J., Cho H., Liaw P.K., Lavernia E.J. A model for the inverse Hall–Petch relation of nanocrystalline materials. *Mater. Sci. Eng. A* (2005) **409**:243-248.
- [5] Dmitriev, A.I., Nikonov, A.Yu., Österle, W. MD sliding simulations of amorphous tribofilms consisting of either SiO₂ or carbon. *Lubricants* (2016) **4**(24):1-12, doi:10.3390/lubricants4030024.
- [6] Ebrahimian-Hosseiniabadi, M., Azari-Dorcheh, K., Moonir Vaghefi, S.M. Wear behavior

- of electroless Ni–P–B₄C composite coatings, *Wear* (2006) **260**:123-127.
- [7] Nikonov, A.Yu., Konovalenko, Iv.S., Dmitriev, A.I. Molecular dynamics study of lattice rearrangement under mechanically activated diffusion. *Phys. Mesomech.* (2016) **19**(1):77–85.
 - [8] Dmitriev, A.I. Nikonov, A.Yu., Psakhie, S.G. Atomistic mechanism of grain boundary sliding with the example of a large-angle boundary $\Sigma=5$. Molecular dynamics calculation. *Phys. Mesomech.* 2011 **14**(1-2):24-31.
 - [9] Dmitriev, A.I., Nikonov, A.Yu., Österle W. Molecular dynamics sliding simulations of amorphous Ni, Ni-P and nanocrystalline Ni films. *Comput. Mater. Sci.*, (2017) **129**:231-238
 - [10] Sheng, H.W., Ma, E. and Kramer, M.J. Relating dynamic properties to atomic structure in metallic glasses, *JOM* (2012) **64**:856-881.
 - [11] Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics, *J. Comput. Phys.* (1995) **117**(1):1-19.
 - [12] Honeycutt, J. and Andersen H. Molecular dynamics study of melting and freezing of small Lennard-Jones clusters. *J. Phys. Chem.* (1987) **91**:4950–4963.
 - [13] Österle W., Dörfel I., Wollschläger N., et al., Potential of different nickel coatings for optimizing the sliding behavior of electrical connectors, *Tribol. Int.* (2017) submitted.
 - [14] Van Swygenhoven, H., Derlet, P.M. and Hasnaoui, A. Atomistic Modeling of Strength of Nanocrystalline Metals. *Adv. Eng. Mater.* (2003) **5**:345–350.